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(54) Title: FUNCTIONAL GROUP CONTAINING ACTIVATED CARBONS

(57) Abstract

A method for producing modified activated carbon materials is provided comprising treating activated carbon material in a halogen containing atmosphere at a temperature of less than 180 °C and treating the resultant product with a nucleophilic agent at elevated temperature. Preferably the halogenation is chlorination, and preferably is carried out at 120 °C or less, more preferably 85 °C or less, and conveniently at 30 °C or less. The nucleophilic agent may be a liquid or a gas, and may be any agent, organic or inorganic, that has a group capable of nucleophilic displacement of the halogen, e.g. chlorine, from the carbon surface. Halogenation is carried out over several, e.g. 24 hours. The present invention relates to the production of activated carbons that have functional groups associated with their surfaces, such that species specificity in adsorption processes may be achieved.

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FUNCTIONAL GROUP CONTAINING ACTIVATED CARBONS.

The present invention relates to the production of activated carbons that have functional groups associated with their surfaces, such that species specificity in adsorption processes may be achieved. Preferred functional groups are borne upon organic chemical moieties.

The present inventors have previously described the production of chlorinated activated carbons that have age resistant properties when exposed to humid air, an agent that can be shown to degrade the materials adsorbent properties over time (Hall and Holmes: Carbon (1992) Vol 2. pp 173-176). By treating activated carbon samples at 180°C for 3 hours in a chlorine atmosphere, followed by washing with water or methanol, they were able to produce materials that at least as effective in adsorbing a model contaminant, trichloronitromethane, as the original activated carbon, even after having been pre-equilibrated by exposure to relative humidity of 80% (w/w). Results suggested that the materials were of enhanced adsorbent activity.

The inventors have now discovered that when the halogenation step of their previous work is carried out at temperatures below the 180°C referred to above, treatment with suitable agents leads to the association of active functional groups borne on moieties contained therein with the carbon surface in such a manner that they cannot be removed by washing or by drying at reduced pressure. Furthermore the present process results in functional group containing carbons that have resistance to ageing in humid atmospheres and which do not produce vapours containing the functional groups in use; the latter allowing immobilisation of volatile agents on the carbon which would be lost if merely applied by normal impregnation procedures.

The result obtained with this relatively low temperature halogenation is in contrast to the result obtained when washes are carried out on carbons that have been treated with chlorine at 180°C or above. The

ability to apply chemical moieties to a carbon surface in this manner provides the highly desirable result of enabling selective activated carbon materials to be produced in a facile and convenient manner with applications, inter alia, as filter materials, gas chromatography adsorbents, catalysts and separator bed components.

Thus in a first aspect of the present invention there is provided a method for producing carbon materials incorporating a functional group comprising halogenating a carbon containing material under conditions such that halogen is incorporated therein but remains displaceable by treatment with a nucleophilic agent, treating the halogenated carbon with a nucleophilic agent bearing the functional group, or a chemical precursor group therefor, to effect displacement of halogen to give a product in which the functional group remains associated with the carbon after heating at reduced pressure and/or washing with aqueous solvents. Particularly preferred materials retain the functional group after heating at a temperature of 120°C and a pressure of 3 mbar.

Fluorine, chlorine, bromine and iodine can all be displaced from the surface of carbon with which they have been reacted. However, bromination must be carried out at relatively high temperature (ca. 200°C) and is difficult to displace, whilst fluorine reacts with the surface and at the same time is absorbed by the carbon. The slow release of absorbed fluorine results in a carbon of low surface stability and introduces a degree of hygroscopic character which is often undesirable. Iodine is difficult to handle and is relatively unreactive. Conversely chlorination may be carried out at low temperatures thus simplifying sample preparation and gas handling procedures. Displaceable chlorine is provided in significant amounts depending upon the temperature of chlorination and is replaced with relative ease by contacting it with a liquid or vapour form of the nucleophilic agent.

Halogenation is preferably with chlorine or bromine, most preferably

with chlorine. Chlorination is preferably carried out at 120°C or less, more preferably 85°C or less, and conveniently at 30°C or less, and is carried out, preferably, from 1 to several hours eg. 24 hours.

The nucleophilic agent may be a solid, liquid or gas, and may be any agent, organic or inorganic, that includes a group capable of displacement of the halogen from the carbon surface. It will be realised that while the term nucleophilic agent is used herein, the precise nature of the association of the agent with the carbon, and displacement of halogen, has not yet been elucidated and thus no limitation on the mechanism of reaction is placed upon the method of the present invention.

Thus while halogen is thought to be displaced from the carbon surface by the action of the nucleophile, it uncertain whether any is retained as a salt with the nucleophilic agent or whether it is lost under vacuum. The characterising feature of the present invention is that the nucleophilic agent, and thus the functional groups thereon, are retained on the carbon at reduced pressure and elevated temperature after such halogen pretreatment whereas without that it is not so retained and thus in time suffers loss of functional group content.

Association of functional group bearing moieties with the carbon is increased with temperature in the displacement step, preferably being the reflux temperature of a liquid nucleophile or about 200°C.

Examples of suitable nucleophilic agents are those of formula (I):



wherein X is oxygen, nitrogen or sulphur; each R is independently selected from H and optionally substituted alkyl or alkenyl groups, or two or more groups R include or form together one or more optionally substituted cycloalkyl, cycloalkenyl or heterocyclic groups; and n is

equal to the valency of atom X minus 1 (with respect to the bond H-X).

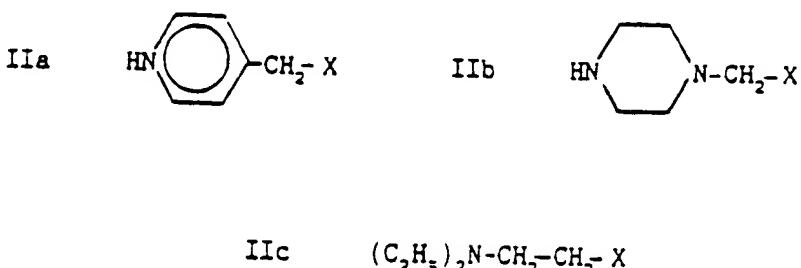
The functional groups to be associated with the carbon, or chemical precursors of these, will depend upon the properties desired of the end product modified carbon, and may include hydrophobic moieties, but most commonly will be groups such as amino, thiol, sulphonic or other sulphur oxide, halogen, carboxy, keto, aldehyde groups or groups specifically capable of being loaded with metal ions or atoms. Other functional groups such as those taking the form of heterocyclic rings may also be substituents, e.g. pyridine and piperidine rings. The term chemical precursor as used here is intended to cover a moiety that is capable of undergoing chemical conversion to a desired group, e.g. by oxidation or reduction, once associated with the carbon surface.

Particular examples of agents that are capable of associating with a carbon pretreated with a chlorine at low temperature to leave a substituted carbon surface resistant to outgassing at reduced pressure and elevated temperature in that they leave functional groups thereon, include alcohols or amines, e.g. methanol, ammonia, ethanolamine, ethylamine, ethylene diamine and isopropylamine.

In order to provide a given functional group on the carbon it will be desired to use a nucleophile that includes a moiety or moieties bearing the given group or its precursor, as well as a nucleophilic group which is used to achieve the association with the carbon. In order to associate desirable groups such as those contained in pyridine, piperazine or triethylamine moieties to a carbon, the nucleophile used may comprise such a moiety linked to a nucleophilic group by a spacer. This strategy is particularly applicable where steric problems may be encountered with a nucleophilic group such as that represented by the opposing nitrogens in piperazine.

For example, pyridine, piperazine and triethylamine moieties may be associated with carbon using the method of the present invention by

use of a compounds of Formula II a-c respectively as the nucleophile wherein X is OH or NH<sub>2</sub> or -SH in each case.



It will be realised that water may be used as a nucleophilic agent although the effect of hydroxy substituents on the carbon would be deleterious for most uses, including use as a filter agent for most noxious materials.

Where the nucleophilic agent is a gas it is preferred to treat the halogenated carbon by flushing it with the gas in neat form, preferably at elevated temperature. This may be carried out immediately after halogenation but it is preferred to de-gas the material of halogen first. In a convenient method of the invention the cooled halogenated carbon is flushed with the nucleophilic gas and is then heated up to a treatment temperature gradually by ramping, e.g. at about 5°C per minute, before heating at the treatment temperature for a period of some hours, e.g. 3-5 hours, where 1 bar pressure is used.

Where the nucleophilic agent is a liquid it is preferred to reflux this at its boiling point with the carbon, for example in a air-excluded system. Thus where the agent is methanol, ethanolamine, pyridine, isopropylamine, triethylamine or ethylene diamine this method is preferred. Reflux is carried out conveniently for several hours. Where the nucleophilic agent is a solid it will be necessary to gasify it or to dissolve it a solvent in which it can be introduced

to the surface of the carbon.

In all cases it is preferable that the functional group containing carbon product of the invention is washed alternately with acid and alkali and additionally with water to remove all reagents. When this procedure is carried out and the product is degassed under vacuum for several hours it is found that an odourless carbon is provided that shows significant amounts of elemental content corresponding to the nucleophilic agent, eg. nitrogen, where the amines are used.

Embodiments of the method and products of the present invention will now be described by way of illustration only by reference to the following non-limiting Examples. Other embodiments falling within the scope of the present invention will occur to those skilled in the art in the light of these.

EXAMPLE 1.

Carbon modifications were carried out using the procedures of Hall and Holmes, Carbon (1992) Vol 2, pp171-176, except in so far as halogenation temperature and wash composition were varied as described herein. For aging studies the carbons were exposed to relative humidity of 80% in shallow dishes at 45°C for up to one year (see method of Adams et al, (1988) Carbon 26, p451). Methanol was used as nucleophilic agent.

Activated carbon samples (30g) were outgassed in an 8l stainless steel vessel for 3 hours at 180°C, cooled if required to the halogenation temperature, then >99% chlorine gas was introduced at a pressure of about 1 bar. After 24 hours the resultant chlorinated carbons were outgassed (3mbar, 180°C) to constant weight before being washed with the nucleophilic agent (flushed if gas) until the washings were no longer strongly acidic, usually 7 x 100ml, then treated at elevated temperature with a further 100ml for 8 hours, under reflux. Samples were dried to a constant weight at 120°C and 3mbar.

Products and the treatment used to obtain them are described in Table 1 below, wherein PS 1% indicates trichloronitromethane breakthrough time in minutes. Water uptake is after exposure to 80% in w/w %. SCII and BPL are activated carbons from Chemviron Ltd of Belgium.

The fact that the carbons of the invention do not age is postulated to be due to lack of sites available for chemisorption of oxygen and/or water vapour. Nucleophile treatment of carbons halogenated at 180°C or above merely removes strongly adsorbed halogen from the pore structures, whereas with chlorinations below that temperature the present inventors find that nature of the chlorine interaction is different and allows displacement, possibly due to relatively weak chlorine carbon bonding under these conditions, e.g. olefinic complex bonding rather than single covalent bonds. It would appear likely from elemental studies that methyl ether groups are formed when methanol is used as the nucleophile, while carbon nitrogen bonds form with the amine agents and optional carbon oxygen bonds with the ethanolamine. It should be noted that the sum of the carbon and oxygen figures of the elemental analysis remains about the same while its composition varies by temperature of halogenation.

TABLE 1

Carbon/treatment	Weight gain w/w%	Cl 0 w/w%	H <sub>2</sub> O uptake%	PS%
Controls				
SCII	-	0.0 1.1	41.7%	94
SCII *	-	0.0 2.2	41.4	69
SCII/water wash	0	- -	41.8	95
BPL	-	0.0 2.0	35.4	97
BPL/*	-	0.0 3.2	35.5	80
*=aged				
180°C				
SCII Cl <sub>2</sub> /water	7.6	8.1 1.0	38.6	112

TABLE 1 (contd.)

Carbon Treatment	Weight gain w/w%	Cl	O w/w%	H <sub>2</sub> O uptake%	PS%
SCII Cl <sub>2</sub> /MeOH	9.7	8.5	1.4	37.2	114
SCII Cl <sub>2</sub> /MeOH*	9.7	-	-	37.5	110
30°C					
SCII Cl <sub>2</sub> /water	4.5	3.7	3.2	41.5	38
SCII Cl <sub>2</sub> /water*	4.5	-	-	41.8	36
BPL Cl <sub>2</sub> /water	2.1	3.3	3.0	34.6	43
SCII Cl <sub>2</sub> /MeOH	6.6	-	-	39.1	65
BPL Cl <sub>2</sub> /MeOH	5.0	-	-	32.6	62

While carbons chlorinated at about 180°C and then extracted with water or methanol have similar adsorption properties, at chlorinations below 180°C the properties are strongly dependent both on the chlorination temperature and the nucleophilic agent used in the displacement step. The methanol treated carbons are much more hydrophobic than the starting materials. None of the chlorinated carbons aged in air, showing that the properties ascribed to 180°C chlorinated carbons previously are retained as chlorination temperature is reduced. This durability is independent of the agent used to treat the chlorinated material.

#### EXAMPLE 2:

BPL and SCII carbons were pretreated as described in Example 1 and then chlorinated at 30°C before being added to ethanalamine or ethylenediamine and heated under reflux for 8 hours. Carbons were decanted and then washed and outgassed as in 1 - 7 below.

1. Acid washes with 10 x 250ml aliquots of 0.1 molar HCl.
2. Base washes with 10 x 250ml aliquots of 0.1 molar NaOH.

3. Water washes with 10 x 250ml aliquots of water.
4. Extractions with 5 x 250ml methanol.
5. Base washes with 5 x 250ml aliquots of 0.1 molar NaHCO<sub>3</sub>.
6. Water washes with 10 x 250ml aliquots of water.
7. Outgassing at 120°C, 3mbar pressure to constant weight.

After extraction and outgassing the carbons were entirely free of odour showing physically absorbed amine to be removed.

The water adsorption properties of the modified carbons were consistent with the presence of additional polar functional groups of secondary amines and hydroxyl or secondary amine with ethylene diamine and ethanolamine as the nucleophilic agent respectively. These modified carbons adsorbed more water at RH values below ca 60% compared to the controls and the water adsorption capacity at high RH (ca. 90-95%) suggested that the modification did not result in significant loss of pore volume. Nitrogen adsorption figures showed that the treatments resulted in less than 10% decrease in total surface area. That the product carbons had a significantly increased content of chemisorbed amine was confirmed by elemental analysis and X-ray photoelectron spectroscopy. See Table 2.

TABLE 2: Elemental analysis for control and chlorinated/aminated carbons % dry carbon weight.

	C%	N%
SCII control	94.0	0.14
BPL control	88.0	0.42
SCII chlorine/ethanolamine	92.6	2.4
SCII chlorine/ethylenediamine	93.0	2.3
BPL chlorine/ethanolamine	86.7	1.82
BPL chlorine/ethylenediamine	86.9	1.95
SCII-direct amination with dimethylamine-Example 3.	96.0	0.49

X-ray photoelectron spectroscopy: XPS showed that significant amounts of chemisorbed nitrogen were present on the carbon surface which was accessible to the X-ray beam (see Table 3); Compared to the controls it can be seen that the technique results in ca. 8 fold increase nitrogen content (SCII nutshell carbon). For the coal based BPL carbon the increase was about three fold, but it should be noted that untreated BPL contains more nitrogen as bought from the supplier.

The chlorinated/ethylenediamine, chlorinated/ethanolamine modified carbons adsorbed certain light gases which are known to react specifically with secondary amines more efficiently from high humidity air compared with control samples. It was also apparent that for ethanolamine the reaction with surface chlorine can take place either with the amine group or the hydroxyl group since the absorption performance of the ethylenediamine modified carbon against the gas was always greater; in this case a free secondary amine group should always be present. Carbons modified with amines (eg. dipropylamine) also absorbed methyl iodide from humid air more efficiently than unmodified controls.

TABLE 3: Quantification of chemisorbed nitrogen by XPS (SCII carbon)

SCII control	Atom %N	0.21	Mass %N	0.2
SCII-chlorinated/ ethylenediamine		1.74		1.4
SCII-chlorinated/ ethanolamine		1.8		1.5
SCII-direct amination dimethylamine (Example 3)		0.4		0.43

Mass % is derived from atomic %

EXAMPLE 3 (Comparative).

Similar experiments to those of Example 2 were performed using dimethylamine with essentially the same outcome. In some cases the carbon was treated with gaseous amine at 600°C but without prior chlorination. XPS and elemental analysis showed the treatment to result in a much smaller increase in nitrogen content compared to those of Example 2 where a chlorination step was included (see Tables 2 and 3). No increase in nitrogen content was observed when the carbon was exposed to the amine at ca. 200°C again without the chlorination step. This correlates well with Example 1 where it is seen that treatment with methanol or water did not affect carbon surface chemistry unless the chlorination step was included.

EXAMPLE 4.

BPL carbons having either ethylenediamine or propylenediamine associated with their surface were prepared using a method as described in Example 2 modified in that the halogenation was carried out at 25°C and the number of bicarbonate washes was reduced to one.

The efficacy of these carbons against a fluorine containing organic compound was measured at a relative humidity of 80% at 22°C at a flow rate of 1.2 litres minutes through a 2cm test carbon bed that had been continuously aged for 16 hours under those conditions. The BPL control gave a relative breakthrough of 7300 over 30 minutes while the ethylenediamine and propylenediamine modified carbons gave a relative breakthrough of 3340 and 1160 respectively; these results illustrating the alteration of protective properties of the carbons after treatment using the method of the invention.

EXAMPLE 5.

BPL carbons having either ethylenediamine or 1,3-diaminopropane (propylenediamine) associated with their surfaces were prepared using a method as described in Example 2 modified in that the

halogenation was carried out at 23°C and that the number of bicarbonate washes was reduced to one.

Association of the respective amines with the carbon was estimated by heating at reduced pressure (0.1mm/Hg) for a period of 2 hours i.e. to constant weight, and then performing elemental analysis. The results of this analysis are given in Table 4 below.

TABLE 4.

SAMPLE	% FOUND C	H	N	S	Cl
BPL 1507 Control	84.48	1.24	0.60	0.88	0.1
BPL 1507/Cl <sub>2</sub> /23°C	74.28	1.16	0.50	0.82	11.3
BPL 1507/Cl <sub>2</sub> /23°C +ethylenediamine	84.57	1.32	2.88	0.72	1.5
BPL 1507/Cl <sub>2</sub> /23°C 1,3-diaminopropane	80.97	1.94	3.52	0.72	1.4

CLAIMS.

1. A method for producing carbon materials incorporating a functional group comprising halogenating a carbon containing material under conditions such that halogen is incorporated therein but remains displaceable by treatment with a nucleophilic agent, treating the halogenated carbon with a nucleophilic agent bearing the functional group, or a chemical precursor group therefor, to effect displacement of halogen to give a product in which the functional group or precursor group is bound such that it remains associated with the carbon after heating at reduced pressure and/or washing with an aqueous solvent or methanol.
2. A method as claimed in claim 1 wherein the functional group remains associated with the carbon after heating at a temperature of 120°C and a pressure of 3 mbar.
3. A method as claimed in claim 1 wherein the functional moiety remains associated with the carbon after washing with an aqueous solvent selected from 0.1 molar HCl, 0.1 molar NaOH and 0.1 molar NaHCO<sub>3</sub>.
4. A method as claimed in claim 1 wherein the halogenation is carried out with chlorine at a temperature less than 180°C.
5. A method as claimed in claim 1 wherein the halogenation is carried out with bromine at a temperature of about 200°C.
6. A method as claimed in any one of claims 1 to 5 wherein the treatment with nucleophilic agent is carried out at an elevated temperature.
7. A method as claimed in any one of claims 1 to 5 wherein the treatment with nucleophilic agent is carried out at a temperature of 20°C to 200°C.

8. A method as claimed in any one of claims 1 to 7 wherein the halogenated carbon is treated with refluxing nucleophilic agent.

9. A method as claimed in any one of claims 1 to 8 wherein the carbon is an activated carbon.

10. A method as claimed in any one of claims 1 to 9 wherein the nucleophilic agent is of formula (I)



wherein X is oxygen, nitrogen or sulphur; each R is independently selected from H and optionally substituted alkyl or alkenyl groups, or two or more groups R include or form together one or more optionally substituted cycloalkyl, cycloalkenyl or heterocyclic groups; and n is equal to the valency of atom X minus 1.

11. A method as claimed in any one of claims 1 to 10 wherein the nucleophilic agent is an amine and/or an alcohol.

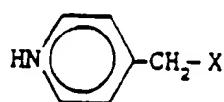
12. A method as claimed in any one of the preceding claims wherein the nucleophilic agent is ammonia, or an organic alcohol and/or organic amine and/or organic thiol which also carries the functional group or precursor group to be associated with the carbon.

13. A method as claimed in claim 12 wherein the nucleophilic agent is selected from the group consisting of methanol, ethanol, ammonia, ethanalamine, ethylamine, ethylene diamine, propylamine, isopropylamine, pyridine and piperazine.

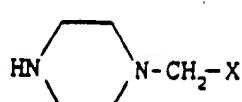
14. A method as claimed in claim 12 wherein the nucleophilic agent includes a pyridine, piperazine or triethylamine group.

15. A method as claimed in claim 12 wherein the nucleophilic agent is selected from groups of Formula IIa, IIb or IIc

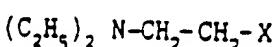
IIa



IIb



IIc



wherein X is OH, -NH<sub>2</sub> or -SH.

16. A carbon material comprising an elemental carbon, having a functional group, or chemical precursor for such group, associated with its surface, said functional group not being removed by heating at reduced pressure and/or washing with an aqueous solvent or methanol.

17. A carbon material as claimed in claim 16 wherein the functional group remains associated with the carbon after heating at a temperature of 120°C and a pressure of 3 mbar.

18. A carbon material as claimed in claim 1 wherein the functional group remains associated with the carbon after washing with an aqueous solvent selected from 0.1 molar HCl, 0.1 molar NaOH and 0.1 molar NaHCO<sub>3</sub>.

19. A carbon material as claimed in claim 13 characterised in that it comprises an activated carbon.

20. A carbon material as claimed in any one of claims 13 to 19 wherein the functional group is an amino, amine, thiol, sulphoxide, halogen, carboxy, sulphonic, keto, aldehyde, piperazine or pyridine moiety.

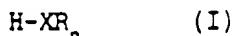
## AMENDED CLAIMS

[received by the International Bureau on 25 November 1994 (25.11.94);  
original claims 1-20 replaced by amended claims 1-18 (3 pages)]

1. A method for producing activated carbon materials incorporating a functional group comprising halogenating an activated carbon under conditions such that halogen is incorporated therein but remains displaceable by treatment with a nucleophilic agent, treating the halogenated activated carbon with a nucleophilic agent bearing the functional group, or a chemical precursor group therefor, to effect displacement of halogen to give a product in which the functional group or precursor group is bound such that it remains associated with the activated carbon after heating at reduced pressure and/or washing with an aqueous solvent or methanol.
2. A method as claimed in claim 1 wherein the functional group remains associated with the carbon after heating at a temperature of 120°C and a pressure of 3 mbar.
3. A method as claimed in claim 1 wherein the functional moiety remains associated with the carbon after washing with an aqueous solvent selected from 0.1 molar HCl, 0.1 molar NaOH and 0.1 molar NaHCO<sub>3</sub>.
4. A method as claimed in claim 1 wherein the halogenation is carried out with chlorine at a temperature less than 180°C.
5. A method as claimed in claim 1 wherein the halogenation is carried out with bromine at a temperature of about 200°C.
6. A method as claimed in any one of claims 1 to 5 wherein the treatment with nucleophilic agent is carried out at an elevated temperature.
7. A method as claimed in any one of claims 1 to 5 wherein the treatment with nucleophilic agent is carried out at a temperature of 20°C to 200°C.

8. A method as claimed in any one of claims 1 to 7 wherein the halogenated carbon is treated with refluxing nucleophilic agent.

9. A method as claimed in any one of claims 1 to 8 wherein the nucleophilic agent is of formula (I)



wherein X is oxygen, nitrogen or sulphur; each R is independently selected from H and optionally substituted alkyl or alkenyl groups, or two or more groups R include or form together one or more optionally substituted cycloalkyl, cycloalkenyl or heterocyclic groups; and n is equal to the valency of atom X minus 1.

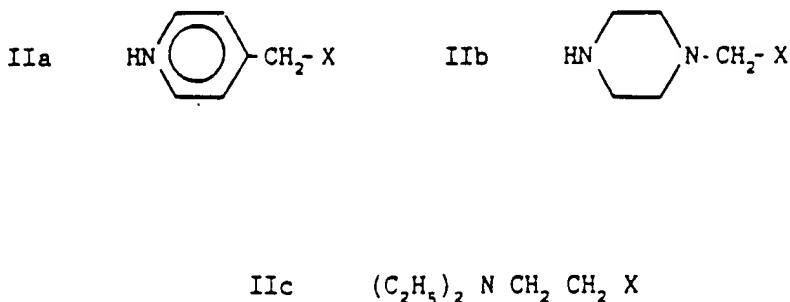
10. A method as claimed in any one of claims 1 to 9 wherein the nucleophilic agent is an amine and/or an alcohol.

11. A method as claimed in any one of the preceding claims wherein the nucleophilic agent is ammonia, or an organic alcohol and/or organic amine and/or organic thiol which also carries the functional group or precursor group to be associated with the carbon.

12. A method as claimed in claim 11 wherein the nucleophilic agent is selected from the group consisting of methanol, ethanol, ammonia, ethanalamine, ethylamine, ethylene diamine, propylamine, isopropylamine, pyridine and piperazine.

13. A method as claimed in claim 11 wherein the nucleophilic agent includes a pyridine, piperazine or triethylamine group.

14. A method as claimed in claim 12 wherein the nucleophilic agent is selected from groups of Formula IIa, IIb or IIc



wherein X is OH, -NH<sub>2</sub> or -SH.

15. An activated carbon material comprising an activated elemental carbon, having a functional group, or chemical precursor for such group, associated with its surface, said functional group not being removed by heating at reduced pressure and/or washing with an aqueous solvent or methanol.

16. An activated carbon material as claimed in claim 15 wherein the functional group remains associated with the carbon after heating at a temperature of 120°C and a pressure of 3 mbar.

17. An activated carbon material as claimed in claim 15 wherein the functional group remains associated with the carbon after washing with an aqueous solvent selected from 0.1 molar HCl, 0.1 molar NaOH and 0.1 molar NaHCO<sub>3</sub>.

18. An activated carbon material as claimed in any one of claims 12 to 17 wherein the functional group is an amino, amine, thiol, sulphoxide, halogen, carboxy, sulphonic, keto, aldehyde, piperazine or pyridine moiety.

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 B01J41/18 801J39/24 801J20/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 031 586 (ROHM AND HAAS) 8 July 1981  see page 10-11; examples 2,3 see page 15; example 9 see page 1-4; claims 1-19 ---	1,4-13, 19,20
A	DE,C,938 308 (BAYER) 28 June 1952 see page 3, line 45-110 ---	1-3,9
A	EP,A,0 486 015 (NIPPODENSO) 20 May 1992 see page 14-15; claims 1-11 ---	1,10
A	FR,A,835 371 (CARBO-NORIT-UNION) 20 December 1938 see page 3; example 3 ---	1,2
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

26 September 1994

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## (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>FR,A,1 086 491 (SPILLMANN) 14 February 1955</p> <p>see page 2, column 1, paragraph 3 - column 2, paragraph 2</p> <p>see page 3; claim 1; example 1</p> <p>-----</p>	1,2,7-10

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		JP-A-	56097552	06-08-81
DE-C-938308		NONE		
EP-A-0486015	20-05-92	JP-A-	4180834	29-06-92
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FR-A-835371		NONE		
FR-A-1086491		NONE		